

# PROPERTIES OF A PHOTOIMAGEABLE THIN POLYIMIDE FILM II.

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## ABSTRACT

The polyimide synthesized from benzophenonetetracarboxylic dianhydride and alkyl-substituted diamines is inherently photosensitive at  $\leq 365$  nm, and a solvent soluble, negative-acting system can be formulated from the fully-imidized resin. The lithographic, thermal, mechanical, and electrical properties of the polyimide films have been characterized. This polyimide film shows good thermal, mechanical, and electrical properties, and a 1:1 aspect ratio is consistently achieved on 10  $\mu\text{m}$  thick films. The thermal properties of the films were determined using TGA and TMA methods. The decomposition temperature was 527°C, the weight loss of the cured film at 350°C in nitrogen was 0.04 %/hour and the thermal expansion coefficient was 37 ppm/°C. The dielectric constant and dissipation factor of the film were 3.0 and 0.003 respectively at 4% humidity. The effects of hard-bake time, hard-bake temperature, nitrogen purge rate during heat treatment, and humidity on the thermal and electrical properties of the thin film were also examined, and are presented here. The rate of weight loss of the cured film increases when the rate of nitrogen purge decreases or when the cure temperature increases. Longer heat treatments resulted in a slight decrease in the CTE and an increase in the  $T_g$ . The electrical properties of the films are dependent both on the humidity during measurement and on the hard-bake temperature.

## INTRODUCTION

Polyimides possess high thermal stability, good chemical resistance, low dielectric constants and excellent planarization capabilities. The combination of these characteristics makes them useful for passivation, alpha particle barriers, stress buffers and interlayer dielectrics in ICs as well as in multilayer thin-film high density interconnect packages[1].

In 1985, J. Pfeifer and O. Rohde of Ciba-Geigy reported the synthesis of a class of solvent soluble polyimides which are based on a benzophenone tetracarboxylic dianhydride (BTDA) and ortho-alkylated diamine polymer backbone, and are inherently photosensitive. They fulfill all the requirements of a storage-stable, high purity, non-shrinking photoimageable polyimide system [2]. These materials are marketed under the trade-name of PROBIMIDE 400 formulations.

The lithographic, mechanical, thermal, and electrical properties of this polyimide thin films have been reported[2-5], and the impact of the processing and cure conditions on the mechanical properties have been examined[5].

This report describes the impact of the processing and cure conditions on the thermal and electrical properties.

## EXPERIMENTAL

The polyimide used in this study was PROBIMIDE 414 (87-707), which is a solution of Probimide 400 polyimide in  $\gamma$ -butyrolactone. The polyimide solution is commercially available from OCG Microelectronic Materials, and was used as received.

Four inch silicon test wafers were coated with Probimide 414 by spin coating 3 ml polyimide solution at spin speed of 1.9 Krpm on a MTI MultiFab wafer track line. The coated wafers were then soft-baked (3 min @ 110°C on hot plate and 30 min @ 110°C in a convection oven under nitrogen), exposed (broad-band, 1200 mJ/cm<sup>2</sup> measured at 365 nm with an OAI Exposure Analyzer, Model 356.), developed and hard-baked for 2 hours at 350°C under nitrogen in a Heraeus hot plate oven. This gave a 10.5  $\mu\text{m}$  thick film after soft bake and 9.5  $\mu\text{m}$  after hard-bake as measured by a Tencor Instruments Alpha-Step 200 Thin Film Measurement System. Polyimide films on wafers were diced into 1/8 inch wide strips using a programmed dicing saw by Micro Automation, Inc., Model 1006, and then removed from the wafers by treatment with buffered ammonium hydrogen fluoride solution at ambient temperature. Strips were rinsed with high-purity DI water and air dried.

The glass transition temperature ( $T_g$ ) and the coefficient of thermal expansion (CTE) of these hard-baked films were measured by a Perkin-Elmer TMA-7 Thermomechanical Analyzer with a 50 ml/min flow

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rate of nitrogen as purge gas. Zinc strips ( $CTE(\text{literature}) = 35 \text{ PPM}/^{\circ}\text{C}$ ) in width of  $1/8$  inch were used to check the overall calibration of the TMA ( $CTE(\text{observed}) = 38 \text{ PPM}/^{\circ}\text{C}$ ).

The onsets of the thermo-decomposition temperatures of the soft-baked, exposed, developed and hard-baked Probimide 414 films were determined using a Perkin-Elmer TGA-7 Thermogravimetric Analyzer with a heating rate of  $10^{\circ}\text{C}/\text{min}$  and a nitrogen purge rate of  $50 \text{ ml}/\text{min}$ . The rate of weight loss was also determined by TGA. Soft-baked, exposed and developed films were heated at a rate of  $3.6^{\circ}\text{C}/\text{min}$  from  $50^{\circ}\text{C}$  to the hard-bake temperature ( $350^{\circ}\text{C}$  or  $400^{\circ}\text{C}$ ), and held at this temperature for 14 hours, which is similar to the heating cycle used for processing in a Heraeus hot-plate oven, and the rate of weight loss was obtained from the weight loss-time curve. The rate of nitrogen purge in these studies was  $0-100 \text{ ml}/\text{min}$ .

Thermal diffusivity, specific heat and thermal conductivity of hard-baked Probimide 414 films were determined by R. Gardner from Sinku-Riko, Inc. The ac calorimetric method which uses a thermal diffusivity meter (Model PR-R1) was used to determine the above thermal properties.

The dielectric constant and dissipation factor of the above hard-baked Probimide 414 films were determined with a Hewlett Packard 4277A LCZ meter. Surface resistivity, volume resistivity and breakdown voltage of Probimide 400 films were determined by A. Agarwal from SRI International.

## RESULT AND DISCUSSION

### The Effect of Processing Parameters on the Thermal Properties:

#### 1. Glass Transition Temperature

Thin films of PROBIMIDE 414 were soft-baked, flood exposed, developed and then hard-baked from 0.5 to 14 hours at  $350$  and  $400^{\circ}\text{C}$  under nitrogen atmosphere. The thin films were removed from wafer, the glass transition temperatures of the sample films were then determined by TMA. The results are given in Figure 1. The increase of hard-bake time from 0.5 to 14 hours resulted in an increase in the  $T_g$ . The increase in  $T_g$  is small at  $350^{\circ}\text{C}$  (e.g.  $10^{\circ}\text{C}$ ), but much larger at  $400^{\circ}\text{C}$ .

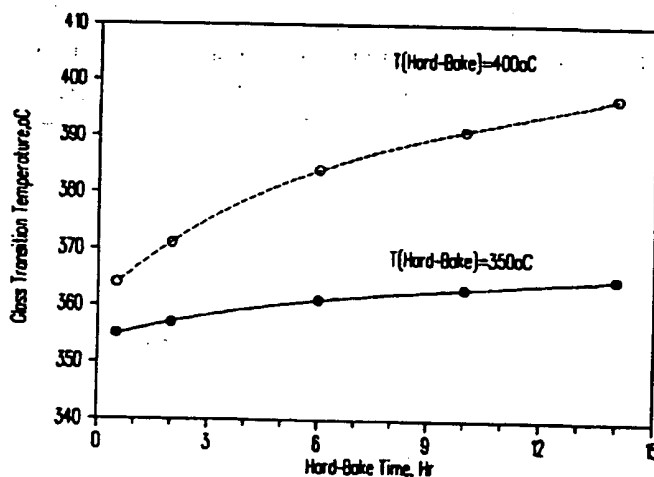
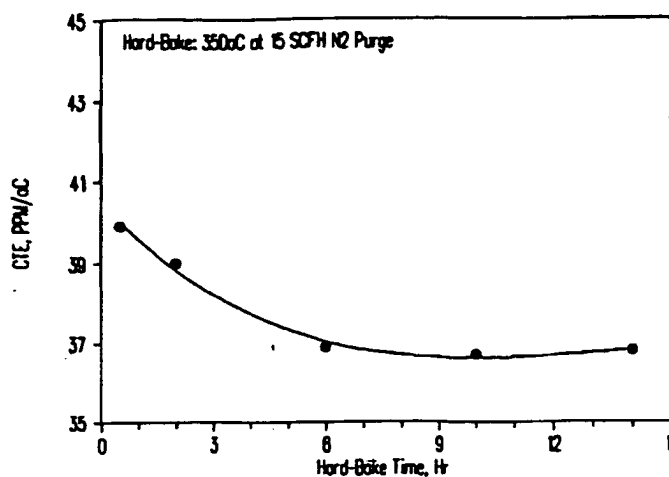


Figure 1.  $T_g$  of hard-baked Probimide 414 films.

#### 2. Coefficient of Thermal Expansion:

CTE values of the above sample films were also determined by TMA, and the results are given in Figure 2. As the hard-bake time increases, a decrease in the CTE value was observed initially, and then reached a constant value of  $37 \text{ ppm}/^{\circ}\text{C}$ . The higher value of CTE for the short-baked film is believed to be due to the presence of lower molecular weight components in the film.

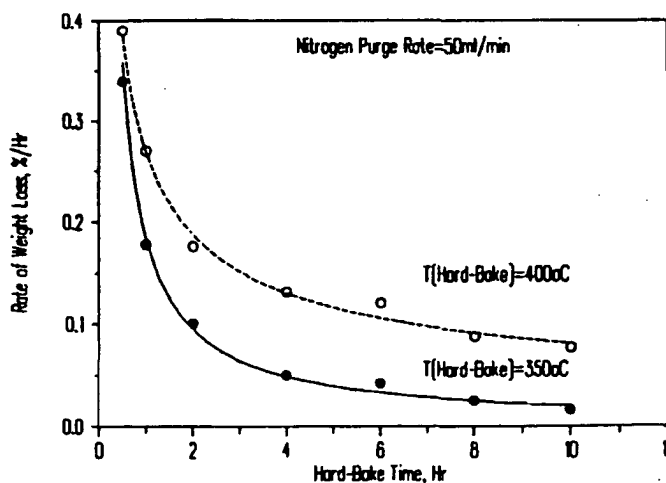
Figure 2. CTE of hard-baked Probimide 414 films



### 3. Rate of Weight Loss:

Thin films of Probimide 414 were soft-baked, exposed, developed and then peeled off from the wafers. The thermal stability of the films was analyzed by TGA. The procedures for the hard-bake process were used here. Sample films were purged with nitrogen for thirty minutes at room temperature, heated up to the hard-bake temperature at a rate of  $3.6^{\circ}\text{C}/\text{min}$ , and then held at the hard-bake temperature for 14 hours under nitrogen atmosphere. The rate of weight loss was obtained from the slope of the weight-time curves. The results are shown in Figure 3 and 4. The rate of weight loss was high in the first half hour due to the loss of the residual solvent, and reached a constant level after more than two hours at the hard-bake temperature. Similar changes in the rate of weight loss were also found for higher hard-bake temperature.

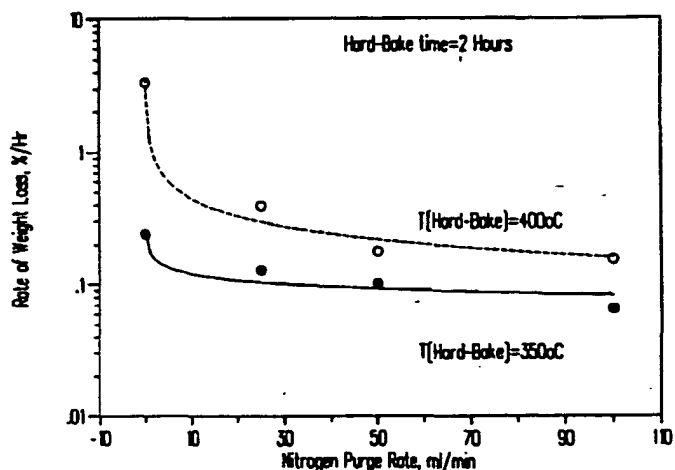
Figure 3. TGA analysis of Probimide 414 films in a nitrogen atmosphere



Probimide 400 is a pre-imidized polyimide resin in  $\gamma$ -butyrolactone. This study shows that it takes more than 0.5 hour at 350°C to remove all the residual low molecular weight components from the sample films. The presence of these volatile components may contribute to the higher CTE and lower  $T_g$  for the polyimide films.

When the films were heated at the hard-bake temperature under various nitrogen purge rates, the rate of weight loss after two hours heat treatment were given in Figure 4. As the nitrogen purge rate decreases, there was an increase in the rate of weight loss observed, which reached a very high value under ambient conditions. Our earlier studies in the mechanical properties of the hard-baked films also showed similar sensitivity to the curing environment, where the mechanical properties were highly depended on the curing environment. Improved mechanical properties were obtained for films hard-baked at higher nitrogen purge rate.

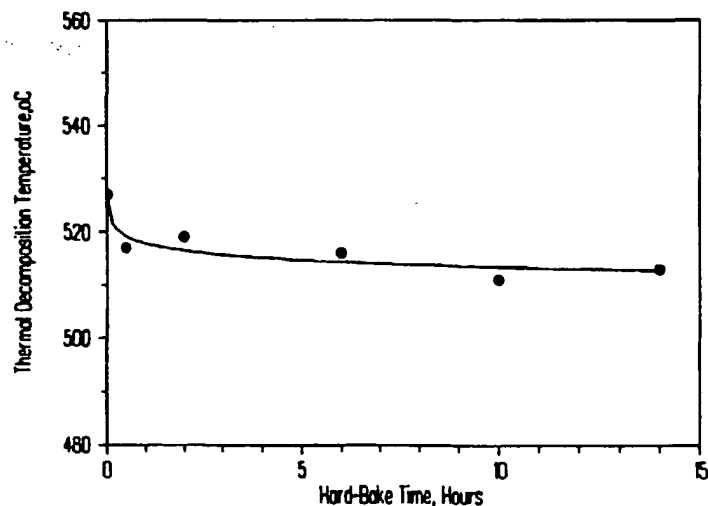
Figure 4. Effect of nitrogen purge rate on the thermal stability of Probimide 414 films



#### 4. Thermal Decomposition:

Thin films of Probimide 414 were soft-baked, exposed, developed and then peeled off from the wafers. The thermal stability of the films was analyzed by TGA, and the results are shown in Figure 5. The polymer film also showed good thermal stability, and degradation occurs at 527°C. The thermal decomposition temperature also remained fairly constant for films which were hard-baked from 0.5 to 14 hours at 350°C.

Figure 5. Thermogravimetric Analysis of Probimide 414 Films



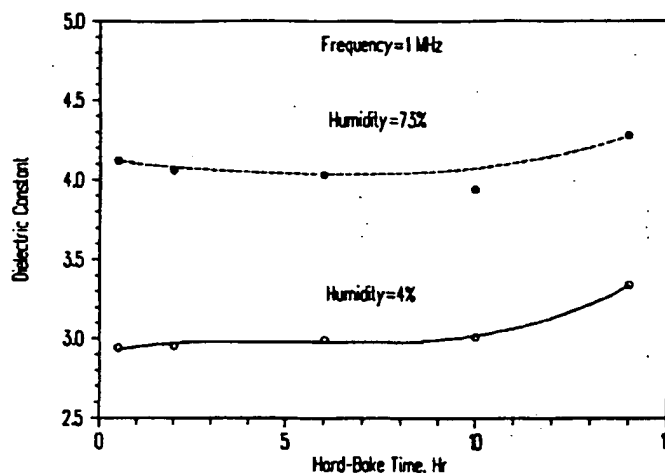
### 5. Thermal Diffusivity, Specific Heat and Thermal Conductivity

The specific heat, thermal diffusivity and thermal conductivity of the hard-baked Probimide 414 films was reported to be 0.32 cal/g/°C, 0.0104 cm²/s and 41E-4 cal/cm/s/°C, these values are comparable to those of other polyimides.

### 6. Electrical Properties:

Thin films of PROBIMIDE 414 on high conductivity wafers were soft-baked, exposed, developed and then hard-baked at 350 and 400°C from 0.5 to 14 hours under nitrogen atmosphere. Aluminum dots were evaporated onto the hard-baked film through a shadow mask to form capacitors, and the electrical properties of these hard-baked films were analyzed at a humidity of 4% and 73%, and the results are given in Figure 6. For polyimide films which were hard-baked at 350°C from 0.5 to 10 hours, the dielectric constant of these films maintained constant at 3.0 under dry condition (% Humidity=4), but increased to a higher, constant value of 4.0 under wet condition (% Humidity=73%). All the measured dielectric constants fluctuated less than 1% over test frequencies from 10 kHz to 1 MHz. The dissipation factor is relatively constant between 0.003 to 0.006 under dry conditions, and reaches a higher values between 0.011 to 0.013 under wet conditions.

Figure 6. Electrical properties of Probimide 414 films. (Frequency=1MHz)



Surface and volume resistivity of Probimide 408 films (film thickness = 1.90 μm) were reported to be 1.2E+18Ω and 8.6E+18Ω-cm. The dielectric strength of Probimide 408 films and Probimide 412 films (film thickness = 9.25 μm) were found to be 3.34E+6 and 2.53E+6 volts/cm. The electrical properties of these Probimide films are comparable to those of other polyimides.

### CONCLUSION

Probimide 400 materials are a class of solvent soluble polyimides which are based on a benzophenone tetracarboxylic dianhydride (BTDA) and ortho-alkylated diamine polymer backbone, and are inherently photosensitive.

The lithographic and mechanical properties of this polyimide have been reported earlier. Patterns with a 1:1 aspect ratio can be obtained from this photosensitive polyimide with vertical developed profiles. The cured film possesses very good mechanical properties. The mechanical properties of the polyimide films does not depend on the level of exposure energy (from 0 to 2 J/cm²). Excellent retention of the

mechanical properties was obtained for thin films which were hard-baked at 350°C at a nitrogen purge rate of 15 SCFH. However, reduced mechanical properties were obtained for films which were hard-baked under low flow rates at either ambient or reduced pressure.

Unlike conventional polyamic acid coatings, the solvent content in the sample films was approximately 5-6% after the soft-bake process, which reduces to 1-2% at even higher soft-bake temperatures (e.g. 170°C). The solvent content in the film increases to 15-20% during the development process. There is much less change in both film thickness and feature dimensions after hard-bake compared to polyamic acids, and a vertical developed profile results.

Thermal properties of the cured Probimide 414 thin films have been analyzed by TMA and TGA. As the hard-bake time increases, an increase in the glass transition temperature is observed. The increase in  $T_g$  was small at 350°C hard-bake temperature, and was higher at 400°C hard-bake temperature. The CTE of the hard-bake films reaches to a constant value of 37 ppm/°C at a hard-bake time of more than four hours; films hard-baked at a shorter times showed slightly higher values of CTE. The onset of the decomposition temperature is 527°C. Although Probimide 400 resin solution is a pre-imidized polyimide resin in  $\gamma$ -butyrolactone, where most of the solvent (e.g. >95%) is removed from the polyimide film during the soft-bake process, it takes heat treatment at 350°C for more than two hours to remove the residual low residue volatile components from the polyimide film. The presence of these volatile components in the film will result lower  $T_g$ , higher rate of weight loss and higher CTE.

For films which were hard-baked at 350°C, the rate of weight loss under isothermal heat treatment at 350°C was low (e.g. 0.04 ppm/°C) under high nitrogen purge conditions. However, the rate of weight loss increases sharply under ambient air. The loss of thermal stability is believed to be due to thermal oxidative degradation of the films.

Excellent retention of the electrical properties is obtained for thin films which are hard-baked at 350°C at a nitrogen purge rate of 15 SCFH. The hard-baked films possess a low dielectric constant of 3.0 in a dry environment, however, the dielectric constant increases to 4.0 as the relative humidity increases to 73%.

These results show that this material has excellent mechanical, thermal and electrical properties for use in multi-chip modules.

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